

Origins of Relative Acidity: First and Second Period Hydrides

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ABSTRACT

The origins of the trends of relative acidity across and between the first and second period hydrides (BH_3 , CH_4 , NH_3 , H_2O , HF , AlH_3 , SiH_4 , PH_3 , H_2S , and HCl) were investigated using molecular and subsystem quantum mechanics at the Hartree-Fock (HF)/6-31++G**//HF/6-31++G** level of theory. The total deprotonation energies, ΔE_{acid} , are interpreted in terms of three component processes: ΔE_1 , deprotonation without electronic and nuclear relaxation; ΔE_2 , electronic relaxation within the acid geometry; and ΔE_3 , nuclear relaxation. ΔE_1 is given from the electrostatic potential at the acidic proton, $\Delta E_1 + \Delta E_2 (= \Delta E^*)$ is given from the calculated energy of the conjugate anion at the acid geometry. The increased acidity across a given period is shown to be already mostly an inherent property of the acid. © 1996 by John Wiley & Sons, Inc.

Introduction

Patterns of relative acidity are typically discussed in terms of the charge of the acidic proton, the relative electronegativity of the central atom, and/or the ability of the associated anion to stabilize the resulting negative charge. The generality of these ideas has been challenged by the demonstration that in some systems the relative acidity is an inherent property of the acid, rather than due to any special relative stability of the resulting anion.¹ These studies suggest that delocalization mechanisms within the anion are not entirely responsible for enhanced relative acidities,

a point that has been contested.² Our interest in the relative acidities of hydrocarbons led us to evaluate the degree to which the relative acidities between simple systems could be understood without consideration of delocalization and the effects of geometry relaxation. If the investigation of a wide range of systems is to be done to assess the relative importance of these and other contributions to the relative acidities of molecules, a basic understanding of the relative acidity patterns in systems without these complications is necessary. Such insight would then form the basis for further study of the more complicated systems.

The first and second period hydrides (NH_3 , CH_4 , NH_3 , H_2O , HF , AlH_3 , SiH_4 , PH_3 , H_2S , and HCl) present an appropriate range of molecules. The central atom varies throughout the series with predictable changes in the characteristics of the

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acidic hydrogen and the resulting anion. There should be no complicated electronic mechanisms, and the geometric relaxation of the anion should not be an important factor. There have been a number of theoretical studies of the deprotonation energy, or equivalently, the proton affinity of the anions of first and second period hydrides, but most have used these systems as benchmarks against which to test various computational techniques.³ Notably, De Proft et al. employed density functional theory to study the acidity of the first and second period hydrides, relating the concepts of hardness and softness to trends in acidity across a given period.³ In a recent series of articles on the first period hydrides, the relative proton affinities of the series was related to the electron affinity of the corresponding XH_{n-1} radical.⁴

We calculated and interpreted the energetics of deprotonation of the first and second period hydrides using both molecular and subsystem quantum mechanics as developed within the theory of atoms in molecules.⁵ The theory generalizes quantum mechanics to a subsystem of a total system, that is, an atom or group of atoms, and allows one to partition observable properties into atomic contributions, which are quantitatively additive to yield the properties of the total system. The energy changes were decomposed into the contributions defined within the usual, fixed nucleus Hamiltonian at both the molecular and atomic levels to provide two different viewpoints for the process. This proved to be a powerful tool for interpretation of the physical underpinnings in a number of applications.⁶ The process of deprotonation is further decomposed into hypothetical steps, allowing us to assess the relative importance of the various contributions to the overall energetics.

Methodology

The neutral and deprotonated structures of the hydrides were considered across the first and second periods of the periodic table, from $X = B$ to F and $X = Al$ to Cl . All of the atomic and molecular properties were determined from Hartree-Fock (HF)/6-31++G** wavefunctions determined at conformations optimized using the same level of theory.⁷ The potential energy surfaces were characterized via the determination of the analytical second derivatives, and each structure was found to be a minimum. The zero-point energies are listed in Table I and have been corrected by a

factor of 0.9 for the overestimation of the force constants at this level.⁸ The molecular calculations were performed with the GAMESS program suite,⁹ using the HF/6-31++G** wave functions to determine the properties of the charge distribution and the atomic properties with the AIMPAC suite of programs.¹⁰ The total energy differences compare favorably to those first period Møller-Plesset (MP)4/6-311++G** values reported earlier,⁵ giving confidence in the physical properties produced by this basis set.

The total energy (and its change) is related to the attraction and repulsion potential energies (and their changes) via the virial theorem:

$$E = -\frac{1}{2}V = -\frac{1}{2}(V_{NE} + V_{EE} + V_{NN}), \quad (1)$$

$$\Delta E = -\frac{1}{2}\Delta V = -\frac{1}{2}(\Delta V_{NE} + \Delta V_{EE} + \Delta V_{NN}), \quad (2)$$

where V_{NE} is the nuclear-electron attraction energy, V_{EE} is the electron-electron repulsion energy, and V_{NN} is the nuclear-nuclear repulsion energy. Because the various contributions to the potential energy are well-defined within the HF Hamiltonian and are related to the distribution of nuclear and electronic charges and their Coulombic interactions, the changes in the total energy of a process can be discussed in terms of the changes in the nuclear and electronic distributions and the resulting changes in the interactions between them.

Results

The total molecular energetic changes and the changes in the contributions to the total potential energy upon deprotonation for the first and second period hydrides are listed in Table I. The deprotonation energy, ΔE_{acid} , is a maximum for CH_4 in the first period and a maximum for SiH_4 in the second, falling off rapidly across each period. The removal of a proton from a system is a large change and is reflected in the changes in the potential energy contributions to the overall ΔE_{acid} . Removal of the proton results in a large decrease in nuclear-nuclear repulsion, V_{NN} . The electrons, which do not change in number, are no longer held by the lost proton and expand and result in a decrease in electron-electron repulsion, V_{EE} . In part because of the loss of a proton and in part because of the expansion of the electron cloud, the attraction term, V_{NE} , also diminishes such that the total energy change on deprotonation is much less than that of any one of these components.

The geometry parameters for the acids and anions are listed in Table II. The bond lengths in the acids and the anions decrease across a given period and deprotonation results in a geometric expansion of the resulting anion in all of the cases studied, excluding those acids with only one hydrogen. This increase in the remaining X—H bond lengths is greatest on the left of each period and decreases along the period to the right. Between

the periods, the increase in remaining X—H bond length is greater in the second period than in the first. We see that the more acidic systems, on the right of each period, have much less geometry relaxation than those less acidic systems to the left upon deprotonation.

Interactions between atoms can be quantitatively characterized by the properties at the bond critical point between the nuclei (Table III).¹¹ In

TABLE I.
Molecular Energetics of Neutral and Anionic Structures of First and Second Row Hydrides and Their Anions.

	BH ₃	$\Delta(\text{BH}_2^-)^a$	$\Delta(\text{BH}_2^-)^b$	Δ_{acid}^c
Total <i>E</i>	−26.3935	+0.7367	−0.0560	+0.6807
<i>V</i> _{NE}	−75.4494	+4.8427	+0.4897	+5.3324
<i>V</i> _{EE}	15.2133	−0.7977	−0.3073	−1.1050
<i>V</i> _{NN}	7.4490	−2.5715	−0.3378	−2.9093
<i>V</i>	−52.7870	+1.4734	−0.1120	+1.3614
ΔE		+462.287	−35.141	+427.146
ZPE	15.505			−8.070
ΔE_{acid}				+419.076
	CH ₄	$\Delta(\text{CH}_3^-)^a$	$\Delta(\text{CH}_3^-)^b$	Δ_{acid}
Total <i>E</i>	−40.2022	+0.6919	−0.0003	+0.6916
<i>V</i> _{NE}	−120.0540	+6.4394	+0.1914	+6.6308
<i>V</i> _{EE}	26.1344	−1.2217	−0.0868	−1.3085
<i>V</i> _{NN}	13.5154	−3.8339	−0.1053	−3.9392
<i>V</i>	−80.4042	+1.3837	−0.0006	+1.3831
ΔE		+434.174	−0.188	+433.986
ZPE	26.672			−9.716
ΔE_{acid}				+424.270
	NH ₃	$\Delta(\text{NH}_2^-)^a$	$\Delta(\text{NH}_2^-)^b$	Δ_{acid}
Total <i>E</i>	−56.2011	+0.6756	−0.0012	+0.6734
<i>V</i> _{NE}	−156.0575	+6.9269	+0.2003	+7.1272
<i>V</i> _{EE}	31.5465	−1.2123	−0.0911	−1.3034
<i>V</i> _{NN}	12.1088	−4.3654	−0.1116	−4.4770
<i>V</i>	−112.4021	+1.3491	−0.0023	+1.3468
ΔE		+423.318	−0.753	+422.565
ZPE	20.724			−9.553
ΔE_{acid}				+413.012
	H ₂ O	$\Delta(\text{OH}^-)^a$	$\Delta(\text{OH}^-)^b$	Δ_{acid}
Total <i>E</i>	−76.0313	+0.6471	0.0000	+0.6471
<i>V</i> _{NE}	−199.2878	+7.2090	+0.0402	+7.2583
<i>V</i> _{EE}	37.8853	−1.0786	−0.0178	−1.0964
<i>V</i> _{NN}	9.3399	−4.8452	−0.0228	−4.8680
<i>V</i>	−152.0626	+1.2943	−0.0003	+1.2942
ΔE		+406.062	0.000	+406.062
ZPE	13.053			−7.835
ΔE_{acid}				+398.227

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TABLE I.
(Continued)

	HF	F ⁻	Δ_{acid}
Total <i>E</i>	-100.0243	-99.4186	+0.6057
<i>V</i> _{NE}	-250.6964	-243.4149	+7.2815
<i>V</i> _{EE}	45.3609	44.5777	-0.7832
<i>V</i> _{NN}	5.2872	0.0000	-5.2872
<i>V</i>	-200.0484	-198.8372	+1.2112
ΔE			+380.083
ZPE	5.756		-5.756
ΔE_{acid}			+374.327

	AlH ₃	$\Delta(\text{AlH}_2^+)$	$\Delta(\text{AlH}_2^-)$	Δ_{acid}
Total <i>E</i>	-243.6206	+0.6215	-0.0325	+0.6070
<i>V</i> _{NE}	-609.3111	+7.4610	+0.8837	+8.3447
<i>V</i> _{EE}	108.4396	-1.4792	-0.3815	-1.8607
<i>V</i> _{NN}	13.6304	-4.7388	-0.5313	-5.2701
<i>V</i>	-487.2412	+1.2430	-0.0650	+1.2140
ΔE		+389.997	-20.3941	+380.899
ZPE	10.967			-5.858
ΔE_{acid}				+375.041

	SiH ₄	$\Delta(\text{SiH}_3^+)$	$\Delta(\text{SiH}_3^-)$	Δ_{acid}
Total <i>E</i>	-291.2320	+0.6271	-0.0049	+0.6222
<i>V</i> _{NE}	-736.9664	+8.5008	+0.8146	+9.3154
<i>V</i> _{EE}	133.1001	-1.5656	-0.3814	-1.9470
<i>V</i> _{NN}	21.4025	-5.6813	-0.4428	-6.1241
<i>V</i>	-582.4638	+1.2538	-0.0095	+1.2443
ΔE		+393.512	-3.075	+390.405
ZPE	18.806			-7.200
ΔE_{acid}				+383.205

	PH ₃	$\Delta(\text{PH}_2^+)$	$\Delta(\text{PH}_2^-)$	Δ_{acid}
Total <i>E</i>	-342.4418	+0.5987	-0.0148	+0.5839
<i>V</i> _{NE}	-851.1219	+8.9729	+0.3139	+9.2868
<i>V</i> _{EE}	148.4692	-1.5993	-0.1480	-1.7473
<i>V</i> _{NN}	17.7692	-6.1763	-0.1955	-6.3718
<i>V</i>	-684.8835	+1.1972	-0.0295	+1.1677
ΔE		375.690	-9.287	+366.403
ZPE	14.412			-6.688
ΔE_{acid}				+359.715

	H ₂ S	$\Delta(\text{SH}^+)$	$\Delta(\text{SH}^-)$	Δ_{acid}
Total <i>E</i>	-398.6760	+0.5648	0.0000	+0.5648
<i>V</i> _{NE}	-975.4207	+9.2030	+0.0940	+9.2970
<i>V</i> _{EE}	165.0381	-1.4225	-0.0470	-1.4695
<i>V</i> _{NN}	13.0305	-6.6509	-0.0471	-6.6980
<i>V</i>	-797.3521	+1.1296	-0.0001	+1.1296
ΔE		+354.418	0.000	+354.418
ZPE	9.187			-5.620
ΔE_{acid}				+348.816

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TABLE I.
(Continued)

	HCl	Cl ⁻	Δ_{acid}
Total E	-460.0675	-459.5397	+0.5278
V_{NE}	-1109.9617	-1100.6644	+9.2973
V_{EE}	182.7216	181.5750	-1.1366
V_{NN}	7.1054	0.0000	-7.1054
V	-920.1347	-919.0795	+1.0552
ΔE			+331.200
ZPE	4.087	0.000	-4.087
ΔE_{acid}			+327.113

The total and contributing energies are given in atomic units and have been corrected for the virial defect. The energy differences, ΔE , are in kcal mol⁻¹ and given relative to the neutral molecule. The zero-point energies (ZPE) have been scaled with a factor of 0.9;⁸ the ZPE is given for HX but the last column gives ΔZPE for the total deprotonation process. The deprotonation energy, ΔE_{acid} , includes the ZPE change.

^aThe superscript * denotes the anion at the acid geometry. This column is the difference between the acid and the anion with geometry frozen at that of the acid, that is, deprotonation without geometry relaxation.

^bThis column is the difference between the frozen and relaxed anion, that is, the relaxation of the anion fixed in the acid geometry to the stable geometry.

^cNet change from the acid to the anion in its stable geometry.

the hydrides, the electron density at the bond critical point, a measure of the strength of interaction, increases steadily along each period signaling an increase in covalent bonding interaction.¹² The Laplacian also becomes more negative across the period as the interaction becomes increasingly

shared between the atoms. The same trends are found for the anions; the values are quantitatively lower because the X—H bonds are longer than in the parent hydrides. In the first period, the Laplacian begins as a small negative value with X=B and decreases until it is strongly negative (a covalent or shared interaction) with X=F. The change in interaction can also be seen in the bonded radius (the distance from the nucleus to the bond critical point) across the period, with the distance from X to the critical point increasing and the distance to hydrogen decreasing as the increasing electronegativity of the X atom becomes dominant in the interaction. The second period shows the same trend for $r(\text{H})$, but the rate of change across the period is slower, as one might expect, because of the lesser electronegativity change across the second period.

The atomic view is given by the atomic properties of the acids and anions that are listed in Table IV. The atomic charge of the acidic hydrogen is negative on the left of each period, becoming roughly neutral in CH₄ of the first period and not until somewhere between H₂S and HCl in the second period, and then rapidly becoming more positive as one moves further to the right. The atomic energies, $E(\Omega)$, mirror the populations.

The deprotonation reaction can be further broken down into hypothetical steps to test the importance of particular parts of the process. These steps involve deprotonation without electron relaxation with ΔE_1 , relaxation of electrons without nuclear

TABLE II.
Geometric Parameters within First and Second Row Hydride and Their Anions.

	H—X	H—X—H
BH ₃	1.188	120.000
BH ₂ ⁻	1.238	105.266
CH ₄	1.084	109.471
CH ₃ ⁻	1.097	109.554
NH ₃	0.999	109.286
NH ₂ ⁻	1.016	103.521
H ₂ O	0.943	107.09
OH ⁻	0.948	
HF	0.902	
AlH ₃	1.582	120.000
AlH ₂ ⁻	1.688	96.112
SiH ₄	1.476	109.471
SiH ₃ ⁻	1.519	101.465
PH ₃	1.397	101.102
PH ₂ ⁻	1.425	93.597
H ₂ S	1.328	94.426
SH ⁻	1.337	
HCl	1.266	

All bond lengths are given in angstroms and all bond angles in degrees.

TABLE III.
Bond Critical Point Properties in First and Second
Row Hydrides and Their Unrelaxed and
Relaxed Anions.

First Row					
	$\rho(r)$	$\nabla^2\rho(r)$	ε	$r(\text{H})$	$r(\text{X})$
BH ₃					
H—B	0.184	-0.230	0.302	1.291	0.954
NH ₂ ⁻					
H—B	0.155	-0.101	0.517	1.373	0.968
CH ₄					
H—C	0.285	-1.052	0.000	0.799	1.249
CH ₃ ⁻					
H—C	0.265	-0.878	0.094	0.850	1.223
NH ₃					
H—N	0.386	-1.955	0.050	0.472	1.416
NH ₂ ⁻					
H—N	0.337	-1.588	0.059	0.555	1.365
H ₂ O					
H—O	0.390	-2.479	0.027	0.340	1.443
OH ⁻					
H—O	0.385	-2.059	0.000	0.387	1.404
HF					
H—F	0.393	-3.757	0.000	0.265	1.439
Second Row					
	$\rho(r)$	$\nabla^2\rho(r)$	ε	r_a	r_b
AlH ₃					
H—Al	0.080	0.286	0.025	1.516	1.472
AlH ₂ ⁻					
H—Al	0.062	0.200	0.077	1.653	1.539
SiH ₄					
H—Si	0.119	0.281	0.000	1.449	1.339
SiH ₃ ⁻					
H—Si	0.103	0.233	0.148	1.496	1.375
PH ₃					
H—P	0.165	0.103	0.224	1.383	1.257
PH ₂ ⁻					
H—P	0.147	0.109	0.266	1.410	1.285
H ₂ S					
H—S	0.223	-0.594	0.302	1.199	1.311
SH ⁻					
H—S	0.202	-0.355	0.000	1.242	1.286
HCl					
H—Cl	0.263	-0.905	0.000	0.735	1.658

All values are in atomic units. The properties are determined at the (3, -1) critical point between the atoms; $\rho(r)$, the total charge density; $\nabla^2\rho(r)$, the Laplacian of the charge density; ε , the ellipticity; $r(\text{H})$ and $r(\text{X})$, the bonded radii for H and X, respectively.

reorganization having an energy change ΔE_2 , and finally relaxation of the anion to its stable structure with ΔE_3 .

Table I also lists the deprotonation energy to the anion with the geometry fixed at that of the acid; in terms of the previous steps, this energy change is $\Delta E_1 + \Delta E_2 = \Delta E^*$. The changes in relaxing the structure of the conjugate base from that of the acid to that of the relaxed anion are also summarized in Table I. In all cases, the frozen-geometry deprotonation, ΔE^* , the deprotonation energy to the anion at the acid geometry, is the dominant energetic contribution to the overall deprotonation energy; the energy associated with the relaxation of geometry, ΔE_3 , makes only a small stabilizing contribution to the overall energetics. The relaxation energy is greatest for the hydrides to the left of each period and decreases rapidly across each period. ΔE^* has the same energetic pattern as ΔE_{acid} , with the losses in attraction dominating. The ordering of the ΔE^* are the same as those for ΔE_{acid} , except for BH₃ which has a larger ΔE^* and smaller ΔE_{acid} than CH₄. Geometric relaxation stabilizes the systems by reducing both the electron-electron and nuclear-nuclear repulsions in roughly equal proportions. The important observation is that even in the systems in which geometric relaxation contributes most, the contribution is still a small fraction of ΔE_{acid} .

As has been noted previously,¹ the negative of the electrostatic potential at the position of the acidic proton yields, when multiplied by the charge of the proton, the energy required to remove the proton from the frozen molecular charge distribution. This electrostatic energy is ΔE_1 and is listed in Table V, and is the first step in our hypothetical deprotonation process, the removal of a proton from the fixed electronic charge distribution of the acid. This static deprotonation energy decreases monotonically from the left of the periodic table to the right in both periods, with the first period decreasing somewhat faster than the second. The contributions to the electrostatic potential, also listed in Table V, show that the electronic contribution (a negative contribution) increases across a period due to the increased amount of charge within each system, but that the nuclear contribution (a positive contribution) increases at a greater rate, resulting in a less negative total potential across a period. The decreased potential results primarily from the increased nuclear charge and its closer proximity within the acid, overcoming the increasing influence of the increased amount of electronic charge.

TABLE IV.
Atomic Properties of First and Second Row Hydrides and Associated Anions.

BH ₃	B	H	Sum	BH ₂ ⁻	B	H	Sum
<i>N</i> (Ω)	2.843	1.715	7.988	<i>N</i> (Ω)	4.351	1.815	7.981
<i>E</i> (Ω)	-23.756	-0.880	-26.396	<i>E</i> (Ω)	-23.988	-0.863	-25.714
<i>V</i> _{NEO} (Ω)	-51.731	-1.719		<i>V</i> _{NEO} (Ω)	-54.559	-1.733	
<i>V</i> _{NET} (Ω)	-55.479	-6.649		<i>V</i> _{NET} (Ω)	-57.656	-6.189	
<i>V</i> _{REP} (Ω)	79.665	4.890		<i>V</i> _{REP} (Ω)	98.384	4.465	
CH ₄	C	H	Sum	CH ₃ ⁻	C	H	Sum
<i>N</i> (Ω)	5.756	1.059	9.992	<i>N</i> (Ω)	6.393	1.202	9.999
<i>E</i> (Ω)	-37.622	-0.646	-40.206	<i>E</i> (Ω)	-37.500	-0.670	-39.510
<i>V</i> _{NEO} (Ω)	-88.838	-1.334		<i>V</i> _{NEO} (Ω)	-89.459	-1.408	
<i>V</i> _{NET} (Ω)	-99.647	-5.097		<i>V</i> _{NET} (Ω)	-97.836	-5.196	
<i>V</i> _{REP} (Ω)	24.401	3.805		<i>V</i> _{REP} (Ω)	22.835	3.855	
NH ₃	N	H	Sum	NH ₂ ⁻	N	H	Sum
<i>N</i> (Ω)	8.175	0.609	10.002	<i>N</i> (Ω)	8.374	0.813	10.000
<i>E</i> (Ω)	-54.811	-0.464	-56.203	<i>E</i> (Ω)	-54.4443	-0.542	-55.527
<i>V</i> _{NEO} (Ω)	-134.074	-0.928		<i>V</i> _{NEO} (Ω)	-133.269	-1.102	
<i>V</i> _{NET} (Ω)	-146.486	-3.194		<i>V</i> _{NET} (Ω)	-141.303	-3.814	
<i>V</i> _{REP} (Ω)	3.685	2.265		<i>V</i> _{REP} (Ω)	3.241	2.278	
H ₂ O	O	H	Sum	OH ⁻	O	H	Sum
<i>N</i> (Ω)	9.259	0.371	10.001	<i>N</i> (Ω)	9.463	0.536	9.999
<i>E</i> (Ω)	-75.356	-0.338	-76.032	<i>E</i> (Ω)	-74.963	-0.421	-75.384
<i>V</i> _{NEO} (Ω)	-184.910	-0.652		<i>V</i> _{NEO} (Ω)	-184.288	-0.825	
<i>V</i> _{NET} (Ω)	-195.062	-2.115		<i>V</i> _{NET} (Ω)	-189.311	-2.718	
<i>V</i> _{REP} (Ω)	44.337	1.439		<i>V</i> _{REP} (Ω)	3.938	1.874	
HF	F	H	Sum	F ⁻	F		
<i>N</i> (Ω)	9.766	0.234	10.000	<i>N</i> (Ω)	10.000		
<i>E</i> (Ω)	-99.773	-0.251	-100.024	<i>E</i> (Ω)	-99.442		
<i>V</i> _{NEO} (Ω)	-243.512	-0.466		<i>V</i> _{NEO} (Ω)	-243.415		
<i>V</i> _{NET} (Ω)	-249.243	-1.454		<i>V</i> _{NET} (Ω)	-243.415		
<i>V</i> _{REP} (Ω)	49.689	0.951		<i>V</i> _{REP} (Ω)	44.530		
AlH ₃	Al	H	Sum	AlH ₂ ⁻	Al	H	Sum
<i>N</i> (Ω)	10.615	1.791	15.988	<i>N</i> (Ω)	12.229	1.880	15.989
<i>E</i> (Ω)	-241.403	-0.739	-243.620	<i>E</i> (Ω)	-241.589	-0.712	-243.020
<i>V</i> _{NEO} (Ω)	-567.669	-1.622		<i>V</i> _{NEO} (Ω)	-574.431	-1.624	
<i>V</i> _{NET} (Ω)	-578.295	-10.319		<i>V</i> _{NET} (Ω)	-581.561	-9.679	
<i>V</i> _{REP} (Ω)	95.489	8.840		<i>V</i> _{REP} (Ω)	98.384	8.254	
SiH ₄	Si	H	Sum	SiH ₃ ⁻	Si	H	Sum
<i>N</i> (Ω)	11.027	1.741	17.991	<i>N</i> (Ω)	12.515	1.826	17.993
<i>E</i> (Ω)	-287.978	-0.814	-291.234	<i>E</i> (Ω)	-288.261	-0.785	-290.616
<i>V</i> _{NEO} (Ω)	672.969	-1.667		<i>V</i> _{NEO} (Ω)	-680.520	-1.672	
<i>V</i> _{NET} (Ω)	-688.723	-12.050		<i>V</i> _{NET} (Ω)	-693.012	-11.553	
<i>V</i> _{REP} (Ω)	112.768	10.422		<i>V</i> _{REP} (Ω)	116.490	9.982	

(Continues on next page)

TABLE IV.
(Continued)

PH ₃	P	H	Sum	PH ₂ ⁻	P	H	Sum
<i>N</i> (Ω)	13.151	1.623	18.020	<i>N</i> (Ω)	14.638	1.680	17.998
<i>E</i> (Ω)	-339.947	-0.838	-342.461	<i>E</i> (Ω)	-340.243	-0.808	-341.859
<i>V</i> _{NEO} (Ω)	-800.209	-1.635		<i>V</i> _{NEO} (Ω)	-808.402	-1.640	
<i>V</i> _{NET} (Ω)	-814.595	-12.247		<i>V</i> _{NET} (Ω)	-818.543	-11.643	
<i>V</i> _{REP} (Ω)	134.700	10.569		<i>V</i> _{REP} (Ω)	138.056	10.026	
H ₂ S	S	H	Sum	SH ⁻	S	H	Sum
<i>N</i> (Ω)	15.510	1.245	18.000	<i>N</i> (Ω)	16.633	1.369	18.002
<i>E</i> (Ω)	-397.253	-0.712	-398.677	<i>E</i> (Ω)	-397.377	-0.734	-398.111
<i>V</i> _{NEO} (Ω)	-943.992	-1.420		<i>V</i> _{NEO} (Ω)	-949.947	-1.487	
<i>V</i> _{NET} (Ω)	-955.791	-9.816		<i>V</i> _{NET} (Ω)	-956.060	-1.688	
<i>V</i> _{REP} (Ω)	161.284	8.391		<i>V</i> _{REP} (Ω)	161.305	8.600	
HCl	Cl	H	Sum	Cl ⁻	Cl		
<i>N</i> (Ω)	17.236	0.764	18.000	<i>N</i> (Ω)	18.000		
<i>E</i> (Ω)	-459.557	-0.510	-460.067	<i>E</i> (Ω)	-460.521		
<i>V</i> _{NEO} (Ω)	-1096.912	-1.038		<i>V</i> _{NEO} (Ω)	-1100.674		
<i>V</i> _{NET} (Ω)	-1103.915	-6.047		<i>V</i> _{NET} (Ω)	-1100.674		
<i>V</i> _{REP} (Ω)	184.799	5.026		<i>V</i> _{REP} (Ω)	179.632		

All atomic properties are in atomic units. *N*(Ω) is the population within the atomic basin; *E*(Ω) is the atomic energy. The energetics have been corrected for the virial defect.

Discussion

These studies provide two different, but complementary views of the deprotonation process in the hydrides, a molecular view based upon the

molecular properties and their changes and an atomic view that breaks the molecular properties into the associated atomic contributions. The molecular view is the coupling of the hypothetical reaction steps (listed in Table VI): the removal of the proton from the frozen electronic charge distribution (the intrinsic acidity of the acid), the relax-

TABLE V.
Electrostatic Potential at Acidic Proton in First and Second Row Hydrides

Molecule	Electronic	Nuclear	Total	Δ <i>E</i> ₁
BH ₃	-3.891	2.741	-1.150	+721.6
CH ₄	-4.953	3.826	-1.127	+707.2
NH ₃	-5.412	4.348	-1.064	+667.7
OH ₂	-5.833	4.837	-0.996	+625.0
FH	-6.188	5.280	-0.908	+579.8
AlH ₃	-5.879	4.736	-1.143	+717.2
SiH ₄	-6.798	5.680	-1.119	+702.2
PH ₃	-7.209	6.152	-1.058	+663.9
SH ₂	-7.660	6.650	-1.011	+634.4
ClH	-8.039	7.104	-0.936	+587.3

The electronic and nuclear contributions to the total are also listed. The values for electrostatic potentials are in atomic units; the deprotonation energy to the completely unrelaxed anion, Δ*E*₁, is in kcal mol⁻¹.

TABLE VI.
Energetics of Hypothetical Multistep Deprotonation.

Hydride	Δ <i>E</i> ₁	Δ <i>E</i> ₂	Δ <i>E</i> ₃	Δ <i>E</i> _{acid}
B	+721.6	-259.3	-35.1	+427.1
C	+707.2	-273.0	-0.2	+434.0
N	+667.7	-244.4	-0.8	+422.6
O	+625.0	-218.9	0.0	+406.1
F	+579.8	-199.7		-380.1
Al	+717.2	-327.2	-20.4	+380.9
Si	+702.2	-308.7	-3.1	+390.4
P	+663.9	-288.2	-9.3	+359.0
S	+634.4	-280.0	0.0	+354.4
Cl	+587.3	-256.1		+331.2

Energy differences are in kcal mol⁻¹. Δ*E*₁ is the deprotonation energy without electronic or nuclear relaxation, Δ*E*₂ is the energy of electronic relaxation, and Δ*E*₃ is the energy of nuclear relaxation to the structure of the minimal energy conjugate anion.

ation of the electronic charge into the frozen nuclear framework (the stabilizing ability of the anion), and the relaxation of the nuclei (the stabilization of geometric relaxation). The relative acidity pattern is reflected in the static deprotonation energy for both periods. Except at the electropositive end with BH_3 and AlH_3 , the ΔE_1 term follows the order of the net deprotonation energy, ΔE_{acid} ; that is, from the middle of the Periodic Table on, in moving to the right in both periods the increased acidity is already inherent in the electrostatic potential at the proton. This result extends to the simple hydrides first observed by Siggel and Thomas and then by others of the relative acidities of several types of acids.¹

Electronic relaxation on removing a proton, ΔE_2 , is a large energy term. It is greatest for CH_3^- in the first period and for AlH_2^- in the second, decreasing across the period as the hydrides become more acidic; the stabilizing ability of the anion is least for the most acidic systems. The effects of geometric relaxation are small for the most acidic systems and is largest for the least acidic systems on the left of each period.

This view clearly demonstrates that the relative acidity is an inherent property of the acid and is reflected in the energy required to remove a proton from the fixed charge distribution. Any special stability of the anion plays a much lesser role; the more acidic systems are less stabilized by the relaxation of either the molecular charge distribution or the geometry.

Further comparison between the first and second period acids can be made by construction of a "pseudothermodynamic" cycle as shown in Figure 1.

As the cycle is closed, the deprotonation energies can be related to the energies required to switch the first period atom, A, for the second period atom, B, in the corresponding acid. The

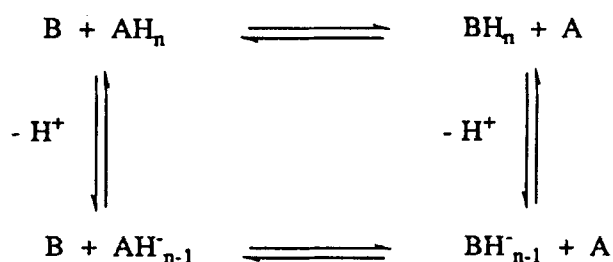


FIGURE 1. The thermodynamic cycle relating deprotonation of a first period acid to deprotonation of the corresponding second period acid.

difference in energy required to swap atom B for A in the acids and anions is equal to the difference in deprotonation between the deprotonation energies for the first and second period acids (Table VII).

$\Delta \Delta E > 0$ for all of the cases, meaning that it is energetically preferable to replace the second period atom for the first in the anions rather than in the acids. While there is a large stabilization from increased attractive energies from swapping A for B, this is overcome by even larger increased repulsion from the large nuclear charge of the second period atom. The change from the first to second period is easier in the anions because there is less nuclear-nuclear repulsion after removal of the proton and geometric expansion of the molecule. Thus, the relatively greater acidity of the second period is primarily due to the increased nuclear-nuclear repulsion experienced by the second period acid rather than a greater stabilization of the corresponding second period anion.

The atomic picture returns a complementary interpretation of the relative acidity patterns in the hydrides. At the atomic level, we can view the deprotonation process in the following way: The ΔE_{acid} is the sum of the hydrogen energy and the energy of the remaining fragment, $|\text{XH}_{n-1}|$, between the acid and anion, depicted in Figure 2.

TABLE VII. Energy Changes Resulting from Hypothetical Cycle Replacing First Row Atoms with Corresponding Atom in Second Row.

	B → Al	C → Si	N → P	O → S	F → Cl
$\Delta \Delta E$	+0.074	+0.069	+0.090	+0.082	+0.078
$\Delta \Delta V_{\text{NE}}$	-3.012	-2.685	-2.160	-2.039	-2.016
$\Delta \Delta V_{\text{EE}}$	+0.756	+0.639	+0.444	+0.373	+0.353
$\Delta \Delta V_{\text{NN}}$	+2.361	+2.185	+1.895	+1.830	+1.818
$\Delta \Delta E^a$	+46.436	+43.298	+56.476	+51.456	+48.946

The energy differences are given in atomic units and have been corrected for the virial defect.

^aThe energy differences, $\Delta \Delta E$ (kcal mol⁻¹), for the process.

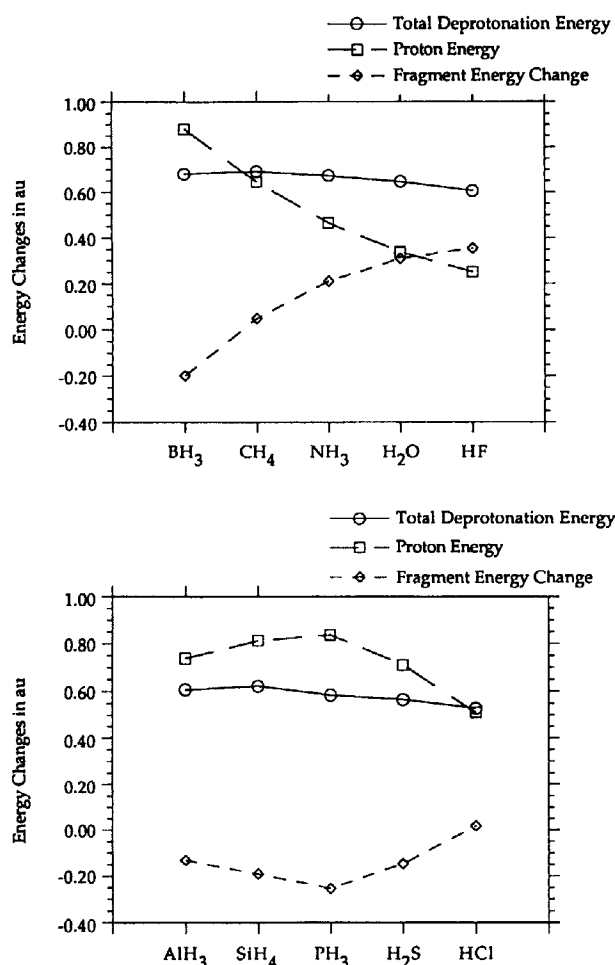


FIGURE 2. Plots of the total deprotonation energy, the hydrogen atom energy, and the energy change of the anionic fragment after deprotonation for the first and second period hydrides.

The energy changes of the fragment, listed in Table VIII, allow us to directly assess the effects of deprotonation upon the rest of the molecule. In this Table: ΔV_{NEO} is the attractive energy between a nucleus and the electronic charge within its own atomic basin and is calculated directly; ΔV_{NET} is the attractive energy between a nucleus and the entire molecular charge density; and ΔV_{REP} is the atomic repulsion energy and is usually obtained by difference. Where hydrogen is more electronegative than X, the energy of the hydrogen atom is greater than the associated ΔE_{acid} and the fragment is stabilized by deprotonation. The large self-stabilization, $\Delta V_{\text{NEO}}(\text{X}^-\text{H}_{n-1})$, resulting from the charge transferred back from the hydrogen, dominates the energy changes for the fragment. In those cases in which X is more electronegative

than H, the hydrogen energy is less than ΔE_{acid} and deprotonation destabilizes the remaining X^-H_{n-1} . These fragments experience large losses in interatomic stabilization from the removal of the proton, as shown by $\Delta V_{\text{NET}}(\text{X}^-\text{H}_{n-1}) \gg \Delta V_{\text{NEO}}(\text{X}^-\text{H}_{n-1})$. The stabilization of the X^-H_{n-1} fragment dominates the ΔE_{acid} for those hydrides in which H is more electronegative than X, the less acidic systems. Once X becomes more electronegative than H, $E(\text{H})$ decreases rapidly and it is this change that determines the overall ΔE_{acid} . This also demonstrates that the relative acidities of the more acidic hydrides are already manifest in the properties of the acids, namely the energy of the hydrogen atom. The relative stabilization of the anion is more important in the least acidic systems, those in which H is more electronegative than X.

Conclusions

This study demonstrates that the relative acidity of the first and second period hydrides is primarily an inherent property of the acid. The dominant energy contribution at the molecular level is the energy required to remove the proton from the fixed distribution of charges. The relaxation of the remaining electronic charge in the anion is most stabilizing in the least acidic systems and least stabilizing in those that are most acidic. Geometric relaxation is relatively unimportant in the energetics of deprotonation. The trends across each period are dominated by the increased nuclear charge of X, as shown in the changes in the potential and the changes in contributions to the overall energetics. The increase in nuclear charge also determines the greater acidity of the second period acids over the first.

The atomic view also shows the relative acidity to be an inherent property of the neutral hydrides, namely the energy of the hydrogen atom. The stabilization of the X^-H_{n-1} fragment dominates the ΔE_{acid} for those hydrides in which H is more electronegative than X, resulting from the transfer of charge to the anion. Once X becomes more electronegative than H, the $E(\text{H})$ decreases rapidly and it is this change that determines the overall ΔE_{acid} . The relative stabilization of the anion is more important in the least acidic systems.

Finally, the atomic view provides the interesting observation that when X and H are roughly

TABLE VIII.
Changes in Properties of Anionic Fragment from Within Acid to Anion.

	BH ₂ ⁻	CH ₃ ⁻	NH ₂ ⁻	OH ⁻	F ⁻
ΔN	+1.718	+1.059	+0.609	+0.371	+0.234
ΔE	-0.198	+0.049	+0.210	+0.309	+0.354
ΔV_{NEO}	-3.278	-0.843	+0.283	+0.371	+0.097
ΔV_{NET}	-1.257	+1.534	+3.733	+5.143	+5.827
ΔV_{REP}	+0.863	-1.447	-3.312	-4.525	-5.120
ΔE^a	-124.247	+30.748	+131.777	+193.901	+222.139
	AlH ₂ ⁻	SiH ₃ ⁻	PH ₂ ⁻	SH ⁻	Cl ⁻
ΔN	+1.792	+1.741	+1.623	+1.245	+0.764
ΔE	-0.132	-0.192	-0.254	-0.147	+0.018
ΔV_{NEO}	-6.646	-7.566	-8.203	-6.022	-3.752
ΔV_{NET}	-1.985	-2.756	-2.960	-0.519	+3.251
ΔV_{REP}	+1.723	+2.351	+2.450	+0.224	-3.214
ΔE^a	-82.831	-120.482	-159.388	-92.244	+11.295

The energy differences are given in atomic units and have been corrected for the virial defect.

^aThe energy differences are in kcal mol⁻¹ for the fragment.

electroneutral, ΔE_{acid} is approximately equal to the energy of the hydrogen atom. This could result in interesting relationships between the energy of the hydrogen atoms and the relative acidities in the hydrocarbon acids.

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